

Prebiotic Homochirality as a Critical Phenomenon

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Abstract. The development of prebiotic homochirality on early-Earth or another planetary platform may be viewed as a critical phenomenon. It is shown, in the context of spatio-temporal polymerization reaction networks, that environmental effects — be them temperature surges or other external disruptions — may destroy any net chirality previously produced. In order to understand the emergence of prebiotic homochirality it is important to model the coupling of polymerization reaction networks to different planetary environments.

Keywords: prebiotic homochirality, origin of life, early planetary environments

1. Introduction

According to the prebiotic soup hypothesis (Wills and Bada, 2000), the early Earth had the supply of organic compounds needed to jump-start polymerization reactions that, through gradual complexification, led to the first biochemical networks displaying some of the characteristics attributed to life, such as metabolic activity and replication. Although the road is still obscure (Orgel, 1998), the situation is not all bleak. In 1953, Stanley Miller simulated tentative conditions of early-Earth in the laboratory to obtain amino acids from simple chemical compounds. That same year, Frank (Frank, 1953) proposed that auto-catalytic polymerization could explain the emergence of biomolecular homochirality, a clear signature of terrestrial and, possibly, all life (Bonner, 1996): terrestrial amino acids belonging to proteins are overwhelmingly left-handed, while sugars are right-handed.

If a bottom-up approach to the early development of life is adopted, the homochirality of life's biochemistry must have emerged dynamically, as reactions among the simplest molecular building blocks occurred with high enough yield. Alternatively, one may assume that, somehow, only monomers of a single chirality were present in the prebiotic soup: they were made that way or brought here during the intense bombardment of Earth's infancy, that lasted to about 3.8 Gyr ago (Gomes *et al.*, 2005). We would, however, still need to understand how homochirality developed elsewhere in the cosmos and not here, and whether it developed with the same chiral bias in more than one place.



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Here, we consider the homochirality of life as an emergent process that took place on early-Earth and, possibly, other planetary platforms. As a starting point, we use the reaction-network model proposed by Sandars (Sandars, 2003), which includes enantiometric cross-inhibition. As shown in the interesting work of Brandenburg and Multamäki (Brandenburg and Multamäki, 2004) (BM), Sandar's polymerization reaction network can be reduced to an effective spatio-temporal mean-field model, where the order parameter is the chiral asymmetry between left and right-handed polymers. To this, we add the effects of an external environment, showing that they can be crucial in the final determination of the net value of enantiometric excess, if any.

2. Modeling Polymerization

Sandars proposed the following polymerization reactions (Sandars, 2003): $L_n + L_1 \xrightarrow{2k_S} L_{n+1}$; $L_n + R_1 \xrightarrow{2k_L} L_nR_1$; $L_1 + L_nR_1 \xrightarrow{k_S} L_{n+1}R_1$; and, $R_1 + L_nR_1 \xrightarrow{k_I} R_1L_nR_1$, where k_S (k_I) are the reaction rates for adding monomers of the same (opposite) chirality to a given chain. The network is completed by adding the four opposite reactions, that is, by interchanging $L \leftrightarrow R$, and by adding a substrate S from which both left and right-handed monomers emerge, $S \xrightarrow{k_C C_L} L_1$ and $S \xrightarrow{k_C C_R} R_1$, where $C_{L(R)}$ determine the enzymatic enhancement of left and right-handed monomers, which is not known. We follow Sandars (2003) and choose $C_L = [L_N]$, $C_R = [R_N]$. As remarked in BM, it is possible to truncate the system to $N = 2$ and still maintain the essential aspects of the dynamics leading to homochiralization. This allows us to model the reaction network as a mean-field theory exhibiting spontaneous chiral symmetry breaking (Weinberg, 1996). Our approach blends the work of BM with the pioneering work of Kondepudi and Nelson, where the reaction network was coupled to time-dependent external effects (Kondepudi and Nelson, 1985): chirality evolves spatio-temporally in contact with an environment.

The equations can be simplified by assuming that the rate of change of $[L_2]$ and $[R_2]$ is much slower than that of $[L_1]$ and $[R_1]$. The same for the substrate $[S]$, so that $d[S]/dt = Q - (Q_L + Q_R) \simeq 0$, where Q_L and Q_R are the source terms for monomers generated from the substrate $[S]$: $Q_L = k_C[S](pC_L + qC_R)$, and $Q_R = k_C[S](pC_R + qC_L)$ (Haken, 1983). The constants $p = \frac{1}{2}(1 + f)$ and $q = \frac{1}{2}(1 - f)$ are given in terms of the fidelity of enzymatic reactions f , an adjustable parameter. As demonstrated by Kondepudi and Nelson (Kondepudi and Nelson, 1983) and many others (Sandars, 2003; Wattis and Coveney, 2005; Saito

and Hyuga, 2004; Gayathri and Rao, 2005; Avetisov and Goldanskii, 1993), auto-catalytic networks show a tendency to bifurcate toward homochirality for values above critical, f_c . The specific value of f_c is model-dependent.

Under the above assumptions, and introducing the dimensionless symmetric and asymmetric variables, $\mathcal{S} \equiv X + Y$ and $\mathcal{A} \equiv X - Y$, where $X \equiv [L_1](2k_S/Q)^{1/2}$ and $Y \equiv [R_1](2k_S/Q)^{1/2}$, BM have shown that the polymerization equations reduce to

$$\lambda_0^{-1} \frac{d\mathcal{S}}{dt} = 1 - \mathcal{S}^2 \quad (1)$$

$$\lambda_0^{-1} \frac{d\mathcal{A}}{dt} = 2f \frac{\mathcal{S}\mathcal{A}}{\mathcal{S}^2 + \mathcal{A}^2} - \mathcal{S}\mathcal{A}, \quad (2)$$

where $\lambda_0 \equiv (2k_S Q)^{1/2}$, with dimension of inverse time. $\mathcal{S} = 1$ is a fixed point: the system will tend towards this value at time-scales of order λ_0 . With $\mathcal{S} = 1$, the equation for the chiral asymmetry has fixed points at $\mathcal{A} = 0$, $\pm \sqrt{2f - 1}$, as pointed out in BM. An enantiometric excess is only possible if $f > f_c = 1/2$.

3. Introducing Environmental Effects

We model the external environment via a stochastic spatio-temporal Langevin equation, rewriting the equations above as

$$\lambda_0^{-1} \left(\frac{d\mathcal{S}}{dt} - k\nabla^2 \mathcal{S} \right) = 1 - \mathcal{S}^2 + \lambda_0^{-1} \xi(\mathbf{x}, t) \quad (3)$$

$$\lambda_0^{-1} \left(\frac{d\mathcal{A}}{dt} - k\nabla^2 \mathcal{A} \right) = 2f \frac{\mathcal{S}\mathcal{A}}{\mathcal{S}^2 + \mathcal{A}^2} - \mathcal{S}\mathcal{A} + \lambda_0^{-1} \xi(\mathbf{x}, t), \quad (4)$$

where k is the diffusion constant and ξ represent white noise with zero mean and a two-point correlation function given by $\langle \xi(\mathbf{x}', t') \xi(\mathbf{x}, t) \rangle = a^2 \delta(\mathbf{x}' - \mathbf{x}) \delta(t' - t)$, and a^2 measures the strength of the external influence. For example, in mean-field models of phase transitions, it is common to write $a^2 = 2\gamma k_B T$, where k_B is Boltzmann's constant, T is the temperature, and γ is a viscosity coefficient. The equations can be made dimensionless by introducing $t_0 = \lambda_0 t$ and $x_0 = \sqrt{\lambda_0/k} x$, which determine the typical spatio-temporal scales in the system. The noise amplitude scales as $a_0^2 \rightarrow \lambda_0^{-1} (\lambda_0/k)^{d/2} a^2$, where d is the number of spatial dimensions. Using as nominal values for the parameters, $k_S \sim 10^{-25} \text{ cm}^3 \text{s}^{-1}$, $Q \sim 10^{15} \text{ cm}^{-3} \text{s}^{-1}$, the diffusivity of water $k = 10^{-9} \text{ m}^2 \text{s}^{-1}$, we obtain, $t \simeq (7 \times 10^4 \text{s}) t_0$ and $x \simeq (1 \text{ cm}) x_0$.

As in BM [see also (Saito and Hyuga, 2004; Gayathri and Rao, 2005)], the concentrations are spatially-dependent quantities. This implicitly assumes that it is possible to define an effective correlation

volume within which the value of the chiral asymmetry \mathcal{A} is fairly homogeneous. (We take $\mathcal{S} = 1$.) Using well-known results from the mean-field theory of phase transitions (Landau and Lifshitz, 1980), we can easily compute the correlation length. From the equation for \mathcal{A} , we obtain an effective potential $V(\mathcal{A})$,

$$V(\mathcal{A}) = \frac{\mathcal{A}^2}{2} - f \ln [\mathcal{A}^2 + 1] . \quad (5)$$

For $f < 1/2$, $V(\mathcal{A})$ has a typical double-well shape, with minima at the fixed points $\mathcal{A}_\pm = \sqrt{2f-1}$. The correlation length, ξ , is given by $\xi^{-2}(\mathcal{A}_{\min}) = V''(\mathcal{A}_{\min})$, where \mathcal{A}_{\min} denotes a minimum of the potential. For the fixed points, we get, $\xi^2(\mathcal{A}_\pm) = f/(2f-1)$. At $f_c = 1/2$ the correlation length diverges, as it should for a critical point. However, the noise parameter a also controls the behavior of the system. Indeed, even if $f = 1$, an enantiometric excess may not develop if a is above a critical value a_c . In analogy with ferromagnets, where above a critical temperature the net magnetization is zero, one may say that above a_c the stochastic forcing due to the external environment overwhelms any local excess of L over R enantiometers within a domain of correlation volume $V_\xi \sim \xi^d$: racemization is achieved at large scales and chiral symmetry is restored throughout space.

4. Numerical Results: Critical Point for Homochirality

Salam (Salam, 1991) suggested that there should be a critical temperature T_c above which any net homochirality is destroyed. However, he conceded that calculating T_c would be quite challenging using the electroweak theory of particle physics. Here, we chose a different route which, we believe, will allow us to explore the qualitative aspects of the problem more effectively: the noise amplitude a may represent a sudden increase in temperature and/or pressure due to a meteoritic impact or volcanic eruption, or, possibly, due to a source of circularly-polarized ultraviolet light (Lucas *et al.*, 2005).

The equation dictating the evolution of the enantiometric excess \mathcal{A} , eq. 3, was solved with a finite-difference method in a 1024^2 grid and a 100^3 grid with $\delta t = 10^{-3}$ and $\delta x = 0.2$, and periodic boundary conditions. In 2d, this corresponds to simulating a shallow pool with linear dimensions of $\ell \sim 200\text{cm}$. We prepared the system initially in a chirally pure phase, which we chose to be $\langle \mathcal{A} \rangle(t = 0) = 1$. The equation is then solved for different values of the external noise, a . As can be seen in Figure 1, for $a^2 > a_c^2 \simeq 0.65(k/\lambda_0)^{3/2}$, $\langle \mathcal{A} \rangle \rightarrow 0$, that is, the system becomes racemized. $\langle \mathcal{A} \rangle$ approaches a constant for

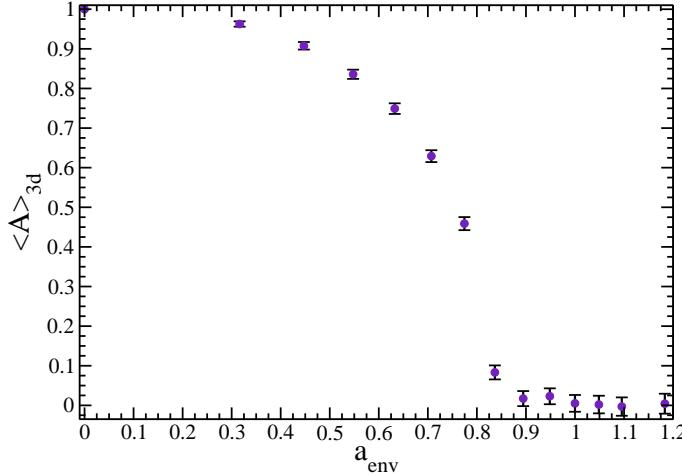


Figure 1. Average enantiometric excess versus “temperature” in three dimensions.

large times, indicating that the reaction network reaches equilibrium with the environment. The results are ensemble averaged. For $d = 2$, $a_c^2 \simeq 1.15(k/\lambda_0)$.

We can describe the environmental impact on homochirality at the microscopic level by introducing the “Ginzburg criterion” familiar of phase transitions (Landau and Lifshitz, 1980). Consider a correlation volume with $\langle A \rangle = 1$ (or -1). What is the energy barrier (E_G) to flip half the molecules in the volume so that $\langle A \rangle \rightarrow 0$? If N_ξ is the number of molecules in a correlation volume, $E_G = (N_\xi/2)E_f$, where E_f is the energy to flip one molecule. The Ginzburg criterion says that this energy is $E_G \simeq V_\xi \Delta V$, where $\Delta V = |V(0) - V(\pm 1)|$. Comparing the two expressions we obtain, $E_f = 2\Delta V(V_\xi/N_\xi)$. From Equation 5, $|V(0) - V(\pm 1)| = 0.193$. Now, $V_\xi \simeq 4\xi^3 = 4(k/\lambda_0)^{3/2}$. (We set $f = 1$.) Using for the microscopic spatial scale $\xi_{\text{micro}} \simeq (Q/k_S)^{-1/6}$, and that $N_\xi \simeq (\xi/\xi_{\text{micro}})^3$, we obtain $E_f \simeq 1.5 \times 10^{-26} \text{ m}^3$. [The energy has dimensions of (length) d .] To complete the argument, we use that the critical “environmental” energy to restore the chiral symmetry was obtained numerically to be (cf. Figure 1), $E_{\text{env}} \simeq 0.65(k/\lambda_0)^{3/2} = 0.65 \times 10^{-6} \text{ m}^3$. We thus obtain the ratio, $E_f/E_{\text{env}} \simeq 2.3 \times 10^{-20}$.

It is tempting to compare this result with possible sources of homochirality. For example, weak neutral currents are expected to induce an excess at room temperature of $g = \Delta E/k_B T \sim 10^{-17}$ (Kondepudi and Nelson, 1983). In the language of the present work, they would

induce a tilt in the potential $V(\mathcal{A})$ proportional to g . Thus, within the violent environment of prebiotic Earth, effects from such sources, even if cumulative, would be negligible: any accumulated excess could be easily wiped out by an external disturbance. Further work along these lines is in progress.

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